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WADD TECHNICAL REPORT 60-782
PART VI

# VAPORIZATION OF COMPOUNDS AND ALLOYS AT HIGH TEMPERATURE

## PART VI.  STUDIES OF THE VAPORS OF THE SYSTEMS Au-Cr AND Au-Pd BY MASS SPECTROMETRY

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*NOVEMBER 1961*

AERONAUTICAL SYSTEMS DIVISION

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# FOREWORD

This report was prepared by the University of Brussels, Belgium, under USAF Contract No. AF 61(052)-225. The contract was initiated under Project No. 7350, "Refractory Inorganic Non-Metallic Materials," Task No. 735001, "Ceramic and Cermet Materials Development." The work was administered under the direction of the Directorate of Materials and Processes, Deputy for Technology, Aeronautical Systems Division, Wright-Patterson Air Force Base, with Mr. F. W. Vahldiek acting as project engineer.

This report covers work conducted from March 1960 to March 1961.

WADD Technical Report 60-782, Part I and Part II, have already been published, Part III and Part V are in preparation, with Part IV to follow when it becomes available.

The authors are grateful to Professor Paul Goldfinger for his great help and encouragement. Dr. Jean Drowart aided us with several useful conversations. Part of the equipment has been made available by the Comité Belge de Spectrométrie de Masse (I.R.S.I.A.).

# ABSTRACT

The molecules Au-Cr and Au-Pd have been identified. From the data for the reaction $Au_2 + X = AuX + Au$, and $D_0^O(Au_2) = 51.5$ kcal/mole:

$$D_0^O(AuCr) = 50.4 \pm 3.5 \text{ kcal/mole}$$

$$D_0^O(AuPd) = 33.3 \pm 5 \text{ kcal/mole}$$

## PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

W. G. RAMKE
Chief, Ceramics and Graphite Branch
Directorate of Materials and Processes

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## INTRODUCTION

Many gaseous molecules containing only "metal" atoms
are known and their spectroscopic and/or thermodynamic
properties measured [1, 2, 3].

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(1) G. Herzberg, Spectra of Diatomic Molecules, (Van Nostrand,
   New-York, 1945).

(2) M.G. Inghram and J. Drowart, in High Temperature
   Technology, Proceedings of an International Symposium;
   (Mc Graw Hill, New-York, 1960).

(3) Ackerman, Stafford and Drowart, J. Chem. Phys. $\underline{33}$, 1784
   (1960) and references cited therein.

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However, among all these molecules, there are none containing
transition element atoms. This has instigated an investigation [4]
on the stability of the homonuclear diatomic transition metal
molecules.

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(4) Verhaegen, Stafford, Goldfinger and Ackerman, XVIII th
   International Congress of Pure and Applied Chemistry,
   Montreal, August, 1961;

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This study indicates special interest in molecules with Cr
and Pd because of the experimental conditions on the one
hand, and their unusual electronic configurations ($d^5 s^1$ and
$d^{10}$) on the other.

The present work reports $D_0^\circ$ (AuCr), $D_0^\circ$ (AuPd), and
measured upper limits of $D_0^\circ$ of $Cr_2$ and $Pd_2$.

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EXPERIMENTAL.

The general experimental set up and procedure already have been described[3,5]. Samples were prepared in situ by melting together weighed quantities of the 99.9% pure metals

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(5) Ackerman, Drowart, Stafford and Verhaegen, J. Chem. Phys. 0000 (preceding article).

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in such proportions as to give approximately equal partial vapor pressures. The samples were contained in either alumina or spinal crucibles[6] placed in a molybdenum Knudsen effusion cell; effusion orifice to sample surface area was about 1 : 50,

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(6) Degussit Al 23 or Sp 23, Degussa, Hanau.

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EXPERIMENTAL DATA.

Ions corresponding to $Au^+, Cr^+, Pd^+, Au^{++}, Cr^{++}, AuCr^+$, and $AuPd^+$ were observed and identified by means of isotopic ratios. When ionized by nominal 70 eV electrons, $I(Cr^{++})/I(Cr^+)$ was observed to be 0.06. Using the ratio of secondary multiplier efficiencies $\gamma(Cr^+)/\gamma(Cr^{++}) \cong 0.5$[7] we have $\sigma(Cr \longrightarrow Cr^{++})/\sigma(Cr \longrightarrow Cr^+) \approx 0.03$

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(7) R.E. Fox, J. Chem. Phys. , 33, 200 (1960)

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Table I presents for the systems Au–Cr and Au–Pd
the measured ratios of ion intensities, corrected for
isotope ratios and for ionization and secondary multiplier
efficiencies. The first column gives the number of the
experiment and the index of point (the data are arranged
in order of increasing temperature); the second column
the absolute temperature; the third the equilibrium constant
for the reaction.

$$X + Au_2 = Au\ X + Au \qquad \Delta H_0^\bullet \tag{1}$$
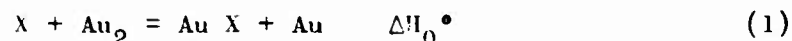
where X is Cr or Pd; the fourth column, $D_0^\bullet(AuX) =$
$$D_0^\bullet(Au_2) - \Delta H_0^\bullet$$

Fig 1 shows $\log \left[ I(Cr^+)I(Au^+)T/I(AuCr^+) \right]$ as a function
of $10^4/T$, where I is the ion current in arbitrary units and
T the absolute temperature.

Table II gives data for calculating upper limits for
$D_0^\bullet(Cr_2)$ and $D_0^\bullet(Pd_2)$. In this case, the third column is
the equilibrium constant for the reaction :

$$X_2(g) = X(g) + X(s, 1) \qquad \Delta H_0^\bullet(a) \tag{1a}$$

The fourth column gives $D_0^\bullet(X_2) = \Delta H_0^\bullet(a) + \Delta H_0^\bullet(vap.X)$

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TREATMENT OF EXPERIMENTAL DATA

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The enthalpy change at $0°K$, $\Delta H_0^\bullet$ for reaction (1) was calculated using the relation

$$\Delta H_0^\bullet = - RT\ln \left[ \frac{I(AuX^+)I(Au^+) \sigma\gamma(Au_2) \sigma\gamma(X)}{\sigma\gamma(AuX) \sigma\gamma(Au)} \bigg/ I(Au_2^+)I(X^+) \right]$$
$$- T \Delta\left[(F^\bullet - H_0^\bullet)/T\right] \qquad (2)$$

where the symbols have the same meaning as in the preceding article[5]. For reaction (1a) the appropriate equilibrium constant and $\Delta(fef)$ were substituted in the right hand side of Eq.(2).

Values for the relative ionization cross sections were taken from Otvos and Stevenson[3] except that of Au which was determined previously[3]. As a check on the calculations for Cr,

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(8) J.W. Otvos and D.P. Stevenson, J. Am. Chem. Soc., 78, 546 (I956).

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the quotient $\sigma\gamma(Cr)/\sigma\gamma(Au)$ was calculated from data for a quantitative vaporization of an alloy containing 249 mg Au and 6I.4 mg Cr. We use the relation

$$\sigma\gamma(X)S' = (S/G)(M/2\pi R)^{1/2} \sum_t I(X)T^{1/2} \Delta t \qquad (3)$$

where S' is characteristic of the instrument; s the effective area of the effusion orifice; G the number of grams of material evaporated; R the gas constant; T the absolute temperature and $\Delta t$ the time increment.

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In the case of a simultaneous vaporization, S' and s cancel. Using the previously determined[3] values of the secondary electron multiplier efficiency $\gamma$ , the calculated ratio $\sigma$ (Cr)/ $\sigma$(Au) is a factor of $1.5 \pm 0.4$ lower than the value inferred from Otvos and Stevenson.

As the difference is just on the limit of being significant, the relative cross section given by the latter authors was used.

For the diatomic molecules it was assumed that the cross section is the sum of cross sections for the atoms[8].

Free energy functions for the gaseous atoms were taken from the compilation of Stull and Sinke[9]. Those of the diatomic molecules were calculated[10] using the estimated interatomic,

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(9) G.C. Stull and D.R. Sinke "Thermodynamic Properties of the Elements." (American Chemical Society, Washington D.C. 1956).
(10) K.S. Pitzer, "Quantum Chemistry" (Prentice-Hall Inc.) Englewood Cliffs, New Jersey, 1953.

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distances, vibration frequencies and electronic multiplicities given in Table III. Although there are numerous empirical formulae[11] relating internuclear distance and vibration frequency,

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(11) See survey by E. Clementi, Ann. Chimi. 50, 548 (1960)

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the necessary parameters are not available for the type of molecules studied here. The interatomic distances used are those given by Pauling[12]. The vibration frequencies for the asymetric molecules were calculated using

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(12) L. Pauling, J. Am. Chem. Soc., 69, 542 (1947); "The
      Nature of the Chemical Bond", Cornell University Press,
      New-York (1960)

Gordy's[13] correlation between electronegativity, inter-
atomic distance and force constant.

(13) W. Gordy, J. Chem. Phys., 14, 305 (1946)

For $Cr_2$ and $Pd_2$ the frequencies were chosen arbitrarily in
keeping with the electronic configuration of the atoms :
$d^5 s^1$ for Cr and $d^{10}$ for Pd[4].

## THE DISSOCIATION ENERGIES

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This is believed to be the first observation of the
molecules AuCr and AuPd. The measured dissociation energies
are given in Table I, the final results being $50.4 \overset{+}{-} 3.5$ and
$33.3 \overset{+}{-} 5$ kcal/mole for AuCr and AuPd respectively. These
are based on the value $D_0^{\circ}(Au_2) = 51.5 \overset{+}{-} 2.2$ kcal/mole. The
absolute uncertainties are estimated using the following
figures.

A 20 % error in internuclear distance or 30 % error
in vibration frequency causes 1.2 kcal/mole error in $D_0^{\circ}$
calculated from measurements made at $1.700^{\circ}$ K.

A 70 % uncertainty is admitted in the ionization
section and secondary electron multiplier efficiency rates.
An uncertainty of $40^{\circ}$ possibly exists between the temperature
measured at the blackbody hole and that which determines
the equilibrium in the cell. Uncertainty in $D_0^{\circ}$ arising
from uncertainty in the multiplicity of the ground and low
lying electronic levels may be quite significant in molecules
formed from atoms with many unpaired electrons. The calculated
dissociation energies may be corrected easily when the

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necessary data become available, noting that the multiplicity m of the ground electronic state enters into $D_0^\bullet$ as $RT \ln m$. If the uncertainty in m is a factor of two as it may well be for AuCr, the resulting uncertainty in $D_0^\bullet$ measured at 1700°K is 2.3 kcal/mole.

From the slope obtained from Fig. 1, and estimated heat capacities, the "second law" $D_0^\bullet(AuCr)$ is calculated to be 52.6 kcal/mole. The result is in good agreement with the "third law" value from Eq.(1). In view of the well known uncertainties in the "second law" measurements made at high temperatures, it is not considered advisable in this case to use comparison between the second and third law to give information on the electronic entropy of AuCr.

The measured upper limits of the partial pressures of $Cr_2(g)$ and $Pd_2(g)$ presented in Table II give upper limits of $D_0^\bullet$ of 40 and 33 kcal/mole respectively. These values are calculated using $\Delta H^\bullet(vap, Cr) = 95.5^{(9,14)}$ and $\Delta H_0^\bullet(vap, Pd) = 84.5^{(15.16)}$ kcal/mole.

(14) O.Kubaschewski and G. Heymer, Acta Meta., 8 416 (1960)
(15) Selected Values for the Thermodynamic Properties of Metals and Alloys, Minerals Research Laboratory, University of California, Berkeley, 1960.
(16) J.F. Haefling and A.H. Daane, Trans. Met. Soc. AIME, 212 115 (1958).

## DISCUSSION

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In both AuCr and AuPd, the forces which cause bonding are considerable and give rise to appreciable bond energies. The 18 kcal/mole difference in the bonding energy between AuCr and AuPd may be correlated with the ground electronic configuration of Cr and Pd atoms. Chromium ($d^5 s^1$, $^7S$) has an unpaired s electron which may combine with the s electron of Au ($d^{10} s^1$, $^2S$), whereas Pd ($d^{10}$, $^1S$) has a quasi-rare gas configuration and bonding is due presumable to interactions with excited states. In keeping with the availability of low lying excited levels of Pd, this interaction is quite effective compared to that in molecules containing Au and other closed sub-shell atom such as Ca or Mg. The dissociation energies of $Au_2Ca_2$ and AuMg are appreciably lower, of the order of 20 kcal/mole[17]

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(17) J. Schiltz, Compt. Rend. 252, 1750 (1961)

J. Ruamps, Ann. Phys. 134, 1111 (1959)

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The greater stability of AuCr relative to AuPd is expected also on the basis of a relation of Pauling[11] which states that single bond energy of XY is the arithmetic mean of the single covalent bond energies of $X_2$ and $Y_2$ plus an "ionic" contribution proportional to $[\chi(X) - \chi(Y)]^2$ where the $\chi$ are electronegativities. On the basis of estimated electronegativity values, AuCr is expected to have much greater ionic stabilization than AuPd. However use of Pauling's relation to estimate the $D_0^{\circ}$ of the symmetric molecules $Cr_2$ and $Pd_2$ is not considered to be reliable.

Fig I
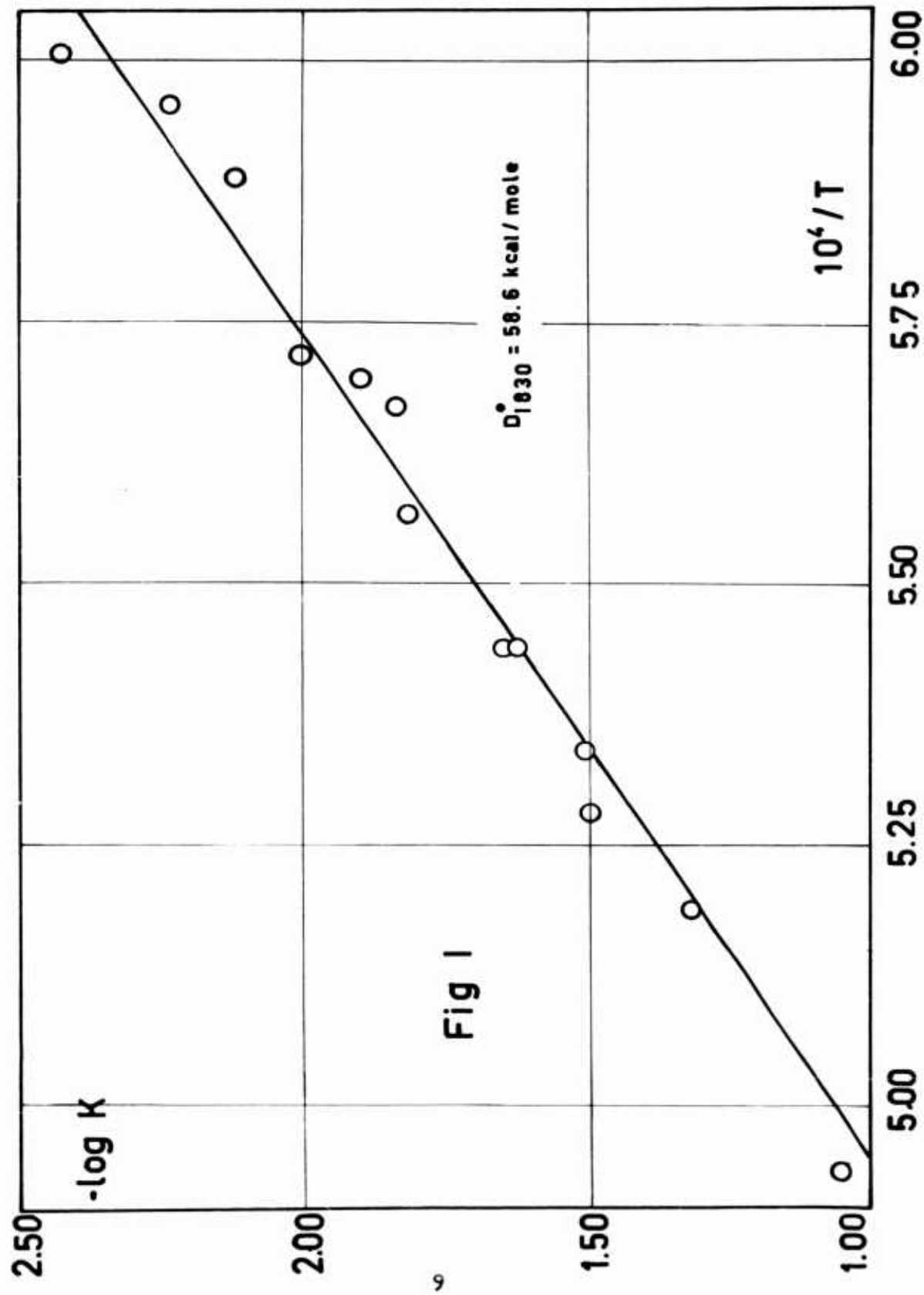
$D^{\bullet}_{1830} = 58.6 \text{ kcal/mole}$

-log K

$10^4/T$

6

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TABLE 1. Measured Pressure Ratios and Calculated Dissociation Energies of AuCr and AuPd.

| Exp. | T°K | $\log \dfrac{p(AuX)p(Au)}{p(Au_2)p(X)}$ | $D_0^{\bullet}$ (AuX) kcal/mole |
|---|---|---|---|
| **AuCr** | | | |
| 3.8 | 1697 | 0.426 | 50.7 |
| 3.12 | 1748 | 0.450 | 50.8 |
| 3.7 | 1780 | 0.412 | 50.5 |
| 3.13 | 1837 | 0.514 | 51.3 |
| 3.6 | 1838 | 0.403 | 50.4 |
| 3.9 | 1873 | 0.447 | 50.8 |
| 3.14 | 1893 | 0.544 | 51.6 |
| 3.10 | 1928 | 0.465 | <u>50.9</u> |
| | | mean | 50.9 |
| 15.7 | 1637 | 0.658 | 50.5 |
| 15.1 | 1670 | 0.101 | 48.2 |
| 15.6 | 1708 | 0.395 | 50.4 |
| 15.2 | 1738 | 0.214 | 49.0 |
| 15.8 | 1739 | 0.585 | 51.9 |
| 15.9 | 1810 | 0.541 | 51.6 |
| 15.3 | 1814 | 0.142 | 48.3 |
| 15.5 | 1831 | 0.240 | 49.1 |
| 15.10 | 1893 | 0.288 | <u>49.4</u> |
| | | mean | 49.8 |
| **AuPd** | | mean of all points | 50.4 |
| 1.1 | 2013 | | |
| 14.1 | 2045 | 1.08 | 33.2 |
| | | 1.04 | <u>33.4</u> |
| | | mean | 33.3 |

$D_0^{\bullet}$ (AuX) $= D_0^{\bullet}(Au_2) - \Delta H_0^{\bullet}$ where $\Delta H_0^{\bullet}$ is for the reaction

$Au_2(g) + X(g) = AuX(g) + Au(g)$ and where $D_0^{\bullet}$ $(Au_2) = 51.5$ kcal/mole

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TABLE II.  Limits of Pressure Ratios and calculated
Dissociation Energies of $Cr_2$ and $Pd_2$

| System | T°K | log $Px/Px_2$ | $D_0^0(X_2)$* |
|--------|------|-------------|-------------|
| Cr | 1909 | 4.93 | 40 |
| Pd | 1920 | 3.55 | 32 |

* $D_0^0(X_2) = \Delta H_0^\bullet(vap.X) - \Delta H_0^\circ$

where $\Delta H_0^\bullet$ is for reaction $X_2(g) \rightarrow X(g) + X(s)$ and
$\Delta H_0^\bullet(vap.Cr) = 95.5$ kcal/mole and $\Delta H_0^\bullet(vap.Pd) = 84.5$ kcal/mole.

TABLE III.  Parameters Used for Calculation of Free Energy
Functions of Diatomic Molecules.

| Molecule | Vibration frequency $cm^{-1}$ | Internuclear distance $\overset{\bullet}{A}$ | Multipli- city M | Relative cross section x Mult. Eff. |
|---|---|---|---|---|
| Au | 191 | 2.68 | 1 | 22.6 |
| AuCr | 250 | 2.44 | 6 | 24.9 |
| AuPd | 200 | 2.60 | 2 | 21.1 |
| $Cr_2$ | 250 | 2.34 | 1 | 44.4 |
| $Pd_2$ | 70 | 2.56 | 1 | 19.5 |